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(54) **Cosmetic compositions**

(57) Cosmetic make-up compositions contain, in a suitable base, at least one coloured pigment resulting from the salification reaction of a polymer carrying salified primary or secondary

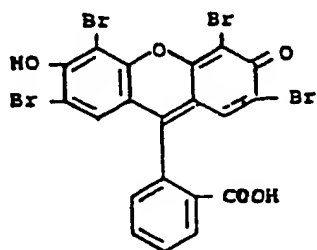
amine groups or quaternised tertiary amine groups with an acid dyestuff in the form of the free acid or its salt, the said dyestuff being fixed in a proportion of at least 10% by weight of the stoichiometric amount. Lipsticks, rouge and nail varnishes are exemplified.

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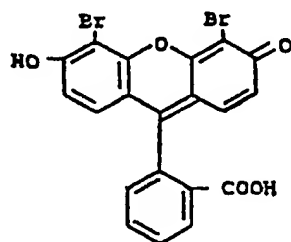
SPECIFICATION

Cosmetic make-up compositions containing, as coloured pigments, a salt of an acid dyestuff and of a polymer carrying salified or quaternised amine groups.

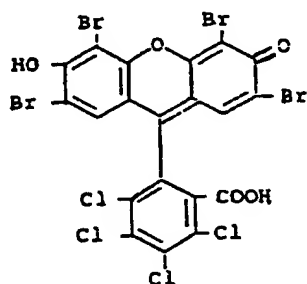
- The present invention relates to cosmetic make-up compositions for the lips, the skin and the nails, such as lipsticks, rouges, make-up foundations and nail varnishes, containing certain coloured pigments as the colouring substance. 5
- All make-up products contain a greater or lesser proportion of a certain number of pigments which can be either inorganic or organic.
- At the same time as colouring the compositions, these pigments give the lips, the skin and the nails a make-up effect, the intensity of which depends on the proportions used. 10
- Numerous organic pigments, better known by the term "lakes", are thus commonly employed in cosmetics for giving the lips, the skin or the nails a make-up effect, these lakes being calcium salts, barium salts, aluminum salts, zirconium salts or other salts of acid dyestuffs such as halogeno acid dyestuff, azo dyestuffs or anthraquinone dyestuffs.
- Amongst these lakes, those which may be mentioned in particular are the ones known under the names D and C Red 21, D and C Orange 5, D and C Red 27, D and C Orange 10, D and C Red 3, D and C Red 7, D and C Red 2, D and C Red 4, D and C Red 8, D and C Red 33, D and C Yellow 5, D and C Yellow 6, D and C Green 5, D and C Yellow 10, D and C Green 3, D and C Blue 1, D and C Blue 2, D and C Violet 1, and the like. 15
- The shades imparted by these various lakes are relatively limited and they do not always make it possible to satisfy the tastes and changes in fashion. 20
- Furthermore, these lakes, or at least a certain number of them, tend to dye the skin, the mucous membrane or the nail keratin superficially.
- This involves the phenomenon better known by cosmeticians under the name "affinity", that is to say the ability which a given colouring substance has to dye the lips, the skin or the nails. 25
- As the regulations in force at the present time are particularly strict as regards use of new lakes, research has naturally been directed towards certain derivatives of the acid dyestuffs of these lakes; thus French Patent No. 1,588,210 describes the use in lipsticks of salts of halogeno acid dyestuffs and of certain amines, such as diethanolamine, triethanolamine, 2-amino-2-methylpropane-1,3-diol, monoisopropanolamine, morpholine and diglycolamine. 30
- Nevertheless, such salts do not make it possible to solve the problems of, on the one hand, obtaining new shades, and, on the other hand, of satisfactorily reducing the "affinity" effect.
- It has now been found that these various disadvantages of the known pigments can be overcome by using a new class of coloured pigments in these make-up compositions, the said pigments resulting essentially from a salification reaction of an acid dyestuff or its salt with a polymer carrying salified primary or secondary amine groups or quaternised tertiary amine groups. 35
- This reaction can be regarded as an ion exchange reaction of the dyestuff with the polymer.
- With the aid of these coloured pigments or coloured polymers, it is possible to develop make-up formulations having shades which were hitherto uncommon, and the "affinity" effect of which is considerably reduced or eliminated totally. 40
- Furthermore, no deterioration in the colouration of the compositions with time has been observed, the colouration of the make-up product being virtually identical to that of the colour imparted to the epidermis or to the nail keratin.
- The present invention accordingly provides a cosmetic make-up composition, more particularly for the lips, the face and the nails, containing at least one coloured pigment in a suitable base, the said coloured pigment resulting from the salification reaction of a polymer carrying salified primary or secondary amine groups, or quaternised tertiary amine groups with an acid dyestuff in the form of the free acid or its salt, the said dyestuff being fixed in a proportion of at least 10% by weight of the stoichiometric amount. 45
- Preferably, the acid dyestuff is fixed in a proportion of 10 to 100%, the proportion of dyestuff fixed depending, of course, on the intensity of the tint which it is desired to obtain. 50
- Amongst the various acid dyestuff capable of leading to the coloured pigments in the compositions according to the invention, there may be mentioned, in particular, those in the lakes such as listed above, and more particularly the following dyestuffs:
- 1) The halogenoacid dyestuffs corresponding to the following formulae: 55



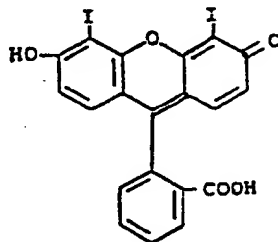
(I)
(D and C Red 21)



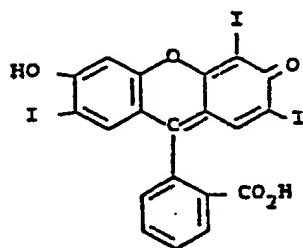
(II)
(D and C Orange 5)



(III)
(D and C Red 27)



(IV)
(D and C Orange 10)

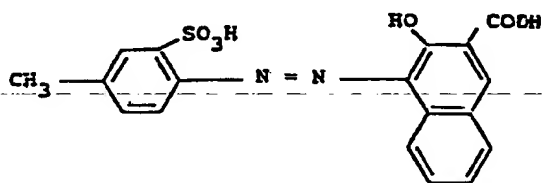


(V)
(D and C Red 3)

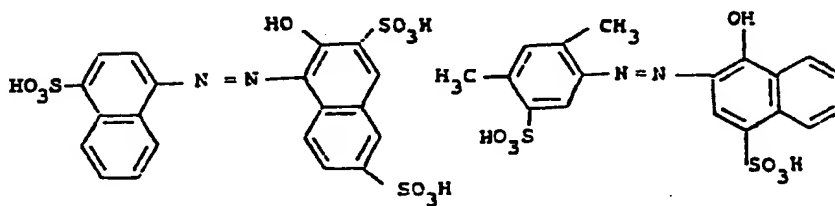
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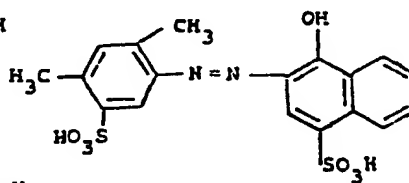
2) The azo dyestuffs corresponding to the following formulae:



(VI)
(D and C Red 7)



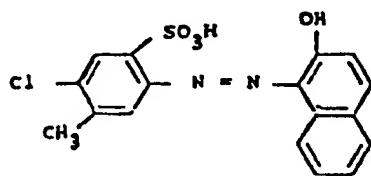
(VII)
(D and C Red 2)



(VIII)
(D and C Red 4)

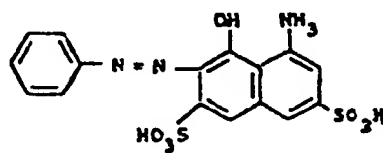
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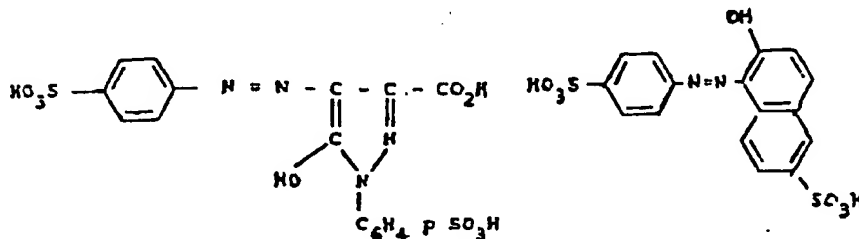
(IX)

(D and C Red 8)



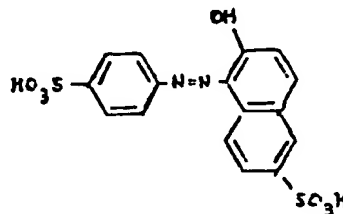
(X)

(D and C Red 33)



(XI)

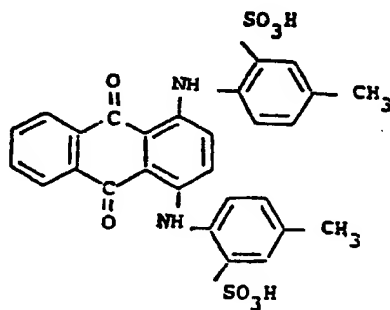
(D and C Yellow 5)



(XII)

(D and C Yellow 6)

5 3) Anthraquinone dyestuffs and especially the dyestuff corresponding to the following formula: 5



(XIII)

(D and C Green 5)

and

4) Acid dyestuffs having a variety of structures, amongst which there may be mentioned those in the lakes D and C Yellow 10, D and C Green 3, D and C Blue 1, D and C Blue 2 and D and C Violet 1. 10

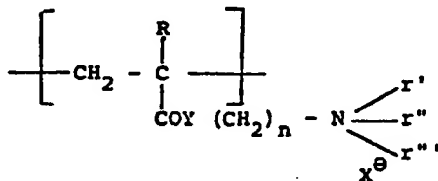
As can be seen, the acid dyestuffs are not solely those containing at least one carboxylic acid group, but can also be dyestuffs carrying one or more sulphonic acid groups or dyestuffs simultaneously carrying at least one carboxylic acid group and at least one sulphonic acid group.

The polymers used carrying salified or quaternised amine groups can also have a variety of structures. Either the polymers can be in the form of homopolymers or copolymers in which the amine groups either form part of the main chain of the polymer or are present in side chains or groups, or alternatively the amine groups are present in a ring which itself serves as a link in the polymer chain. 15

The following may be mentioned amongst the particularly preferred polymers carrying salified primary or secondary amine groups or quaternised tertiary amine groups:

20 1) Polyvinylamine salts, such as polyvinylamine hydrochloride, typically having a weight-average molecular weight of 1,000 to 200,000, preferably 2,000 to 150,000 (average molecular weight determined by light scattering or by gel permeation chromatography). 20

2) Homopolymers or copolymers containing units of the formula:

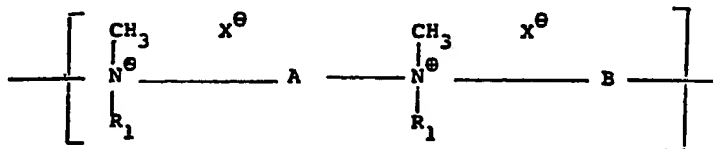


in which: n is 2 or 3, Y is O or NH, R represents a hydrogen atom or the CH₃ radical, r', r'' and r''', which are identical or different, represent an alkyl radical having from 1 to 6 carbon atoms, and X[⊖] is a Cl[⊖], Br[⊖] or CH₃SO₄[⊖] anion.

These polymers typically have a molecular weight of 1,000 to 200,000 and preferably 2,000 to 150,000 (determined by the same methods as above).

Amongst the homopolymers, there may be mentioned, in particular, poly-[2-(N,N-dimethyl-N-ethylammonium)-ethyl methacrylate] bromide and poly-[3-(N,N-dimethyl-N-ethylammonium)-propylacrylamide]bromide, and amongst the copolymers, there may be mentioned those also containing units derived from the polymerisation of unsaturated monomers, such as methacrylates or acrylates, in which the alkyl radical is linear or branched and contains from 1 to 18 carbon atoms.

3) The polymers better known under the name "lonenes", and especially those containing units corresponding to the following formula:

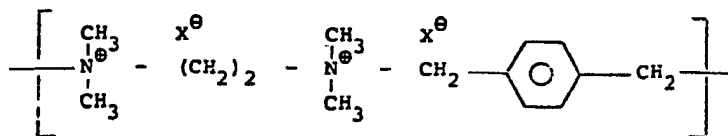


in which: A and B, which are identical or different, either represent a linear or branched alkylene radical having from 2 to 18 carbon atoms, which is optionally substituted by a hydroxyl radical and/or contains a chain oxygen atom or ureido group, or represent an o-, m- or p-xylylene group, R₁ represents an alkyl radical having from 1 to 18 carbon atoms, and X[⊖] is Cl[⊖] or Br[⊖].

These polymers typically have a molecular weight of 1,000 to 50,000, preferably 2,000 to 30,000 (determined by the same methods as mentioned above).

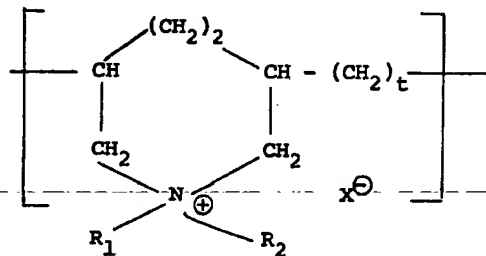
These polymers are described more particularly in French Patents No. 75/15,161 and No. 78/17,899.

Amongst these ionenes, it is preferred, according to the invention, to use the poly-(N,N,N',N'-tetramethyl-N-dimethylene-p-xylylenediammonium) dihalides of the formula:



and in particular poly-(N,N,N',N'-tetramethyl-N-dimethylene-p-xylylenediammonium) dibromide.

4) Cyclic homopolymers or copolymers containing units corresponding to the following formula:



in which: l=0 or 1 such that if l=0, t=1, and if l=1, t=0, R₁ and R₂, which are identical or different represent an alkyl radical having from 1 to 8 carbon atoms, and X[⊖] is Cl[⊖] or Br[⊖].

These polymers typically have a molecular weight of 1,000 to 50,000, preferably 2,000 to 30,000 (determined by the same methods as mentioned above).

Amongst the particularly preferred homopolymers, there may be mentioned, in particular, the one obtained from N,N-dimethyl-N,N-diallylammonium chloride (R₁=R₂=CH₃ and X[⊖]=Cl[⊖]).

If the polymers are in the form of copolymers, the other units may result from the polymerisation of unsaturated monomers such as acrylamide, N-vinylpyrrolidone, vinyl esters, acrylic or methacrylic acid esters.

Amongst the homopolymers and copolymers of this type, there may be mentioned, in particular, those described in French Patents No. 71/06,387, No. 73/23,970 and No. 77/15,088 and also in U.S. Patent 3,862,091, and in particular those marketed under the name MERQUAT.

The coloured pigments or coloured polymers used in the compositions according to the invention can be obtained by reacting a solution of the acid dyestuff or of its salt with a solution or a dispersion of the polymer carrying salified or quaternised amine groups, in an aqueous medium, preferably water,

with stirring, the reaction preferably being carried out at ambient temperature for a sufficient period of time, say 15 minutes to 5 hours, for the dyestuff to become fixed to the basic sites of the polymer.

In order to accelerate the reaction, however, it is possible to heat the mixture to a temperature of, for example, 30 to 60°C.

5 After the reaction, the product obtained can be filtered off and washed with water until the final wash waters are colourless and devoid of residual acidity. 5

The coloured polymer obtained can then be dried, and before being used in a cosmetic composition, ground to a suitable particle size, preferably less than 250 microns.

Analyses carried out on the coloured polymers thus obtained make it possible to show that the 10 fixing of the dyestuff takes place under excellent conditions, the unfixed percentage of the dyestuff 10 sometimes being less than about 1%.

The cosmetic make-up compositions according to the invention can be presented in the form of, 15 for example, sticks, pastes, emulsions, suspensions, dispersions, powders or solutions, and can form 15 lipsticks, mascaras, lip gloss products, rouges, eye shadows, make-up foundations, eye liners, powders or nail varnishes, for example. 15

In the compositions according to the invention, the proportion of the coloured polymer is generally 0.1 to 20% by weight based on the total weight of the composition.

The concentration, of course, depends on the intensity of colouration which it is desired to give the compositions.

20 According to the invention, the coloured polymer can be used in association with inorganic or 20 organic pigments, and especially with lakes, such as those commonly used and listed above.

Suitable inorganic pigments include iron oxides (red, brown, black and yellow), chromium oxides, 25 ultramarines (aluminosilicate polysulphides), titanium dioxide, manganese pyrophosphate and prussian blue (ferric ferrocyanide). These various compounds, singly or in admixture, are generally employed at 25 concentrations of 0.1 to 40% by weight based on the total weight of the cosmetic composition. 25

The compositions can also contain agents for imparting pearlescence, such as bismuth oxychloride, titanium mica and guanine crystals.

If the compositions are presented in the form of sticks and especially in the form of lipsticks, eye 30 shadows, rouges and make-up foundations, they contain a large proportion of fatty substance which 30 can be one or more waxes, for example: ozokerite, lanoline, lanoline alcohol, hydrogenated lanoline, acetylated lanoline, lanoline wax, beeswax, candelilla wax, microcrystalline wax, carnauba wax, cetyl alcohol, stearyl alcohol, cacao butter, lanoline fatty acids, petroleum jelly, vaselines, mono-, di- and tri- 35 glycerides which are solid at 25°C, fatty acid esters which are solid at 25°C, silicone waxes, such as 35 methyl octadecane-oxypolysiloxane and poly-(di-methylsiloxo)-stearoxysiloxane, stearic mono-ethanolamide, colophony and its derivatives, such as the abietates of glycol and glycerol, hydrogenated 35 oils which are solid at 25°C, saccharoglycerides, and the oleates, myristates, lanolates, stearates and dihydroxystearates of calcium, magnesium, zirconium and aluminium.

The fatty substance can also be in the form of a mixture of at least one wax and at least one oil, 40 for example: paraffin oil, purcellin oil, perhydrosqualene, sweet-almond oil, avocado oil, calophyllum oil, 40 castor oil, sesame oil, jojoba oil, mineral oils having a boiling point of 310 to 410°C, silicone oils, such 40 as dimethylpolysiloxanes, linoleyl alcohol, linolenyl alcohol, oleyl alcohol, cereal germ oil, such as wheatgerm oil, isopropyl lanolate, isopropyl palmitate, isopropyl myristate, butyl myristate, cetyl 45 myristate, hexadecyl stearate, butyl stearate, decyl oleate, acetyl glycerides, the octanoates and 45 decanoates of alcohols and polyalcohols, such as those of glycol and glycerol, the ricinoleates of alcohols and polyalcohols, such as cetyl ricinoleate, isostearyl alcohol, isocetyl lanolate, isopropyl 45 adipate, hexyl laurate and octyldodecanol. 45

In general, the fatty substance in these compositions in stick form can represent up to 99.9% by weight of the total weight of the composition.

50 These compositions can also contain other ingredients, such as glycols, polyethylene glycols, 50 polypropylene glycols, monoalkanolamides, non-coloured polymers, inorganic or organic fillers, 50 preservatives or UV filters or other additives customary in cosmetics. 50

These compositions in stick form are preferably anhydrous; however, in certain cases, they can contain a certain amount of water, generally not more than 40% by weight based on the total weight of the cosmetic composition.

55 If the cosmetic compositions according to the invention are presented in semi-solid form, that is 55 to say in the form of pastes or creams, they can be either anhydrous or aqueous and they constitute 55 mascaras, eye liners, make-up foundations, rouges, eye shadows, lipsticks or creams for concealing under-eye circles, for example.

60 If these pastes or creams are aqueous, they are more particularly emulsions of the water-in-oil or 60 oil-in-water type, in which the fatty phase represents from 1 to 98.8% by weight, the water phase from 1 to 98.8% and the emulsifying agent from 0.1 to 30%.

These compositions can also contain other conventional ingredients, such as perfumes, antioxidants, preservatives, gelling agents, UV filters, dyestuffs, pigments, agents for imparting pearlescence, non-coloured polymers and inorganic or organic fillers.

65 When the compositions are presented in the form of a powder, they essentially consist of an 65

Inorganic or organic filler, such as talc, kaolin, starches, polyethylene powders or polyamide powders, as well as additives, such as binders or dyestuffs.

Such compositions can also contain various additives customary in cosmetics, such as perfumes, antioxidants and preservatives.

- 5 When they are presented in the form of nail varnishes, the compositions according to the invention essentially consist of nitrocellulose and of a natural or synthetic polymer dissolved in a solvent system, this solution optionally containing other additives, such as pigments and/or agents for imparting pearlescence. 5

- 10 According to this embodiment, the coloured polymer is suitably present in an amount of 0.1 to 5% by weight. 10

The following Examples further illustrate the present invention, including the coloured pigments.

Preparation of the coloured polymers

Example 1

- 15 A solution consisting of 0.5 g of polyvinylamine hydrochloride and 4.5 g of water is added dropwise, with vigorous stirring, to a solution consisting of 1 g of the sodium salt of the dyestuff D and C Red 33 and 20 g of water. 15

The stirring is continued for 1 hour 30 minutes in the absence of light, the coloured polymer is then filtered off on a glass frit and the product collected is washed several times with water until the wash waters are colourless.

- 20 After drying, the desired salt is obtained with a yield of 65%. 20

The salts of Examples 2 to 9 in the table below were also prepared by following the same procedure as that described in Example 1 above.

Example	Dyestuff	Polymer	Yield %
Ex. 2	D and C Yellow 10 (free acid)	homopolymer of poly-(N,N,N',N'-tetramethyl-N-dimethylene-p-xylylenediammonium) dibromide	55
Ex. 3	D and C Blue 1 (Na salt)	homopolymer of poly-(N,N,N',N'-tetramethyl-N-dimethylene-p-xylylenediammonium) dibromide	90
Ex. 4	D and C Green 5 (Na salt)	MERQUAT 100*	45
Ex. 5	D and C Yellow 5 (Na salt)	Polyvinylamine hydrochloride	55
Ex. 6	D and C Yellow 6 (Na salt)	Polyvinylamine hydrochloride	55
Ex. 7	D and C Yellow 5 (Na salt)	MERQUAT 100	40
Ex. 8 (**)	D and C Red 4 (Na salt)	MERQUAT 100	60
Ex. 9	D and C Yellow 5 (Na salt)	homopolymer of poly-[2-(N,N-dimethyl-N-ethylammonium)-ethyl methacrylate] bromide	45

*MERQUAT 100 (sold by Merck) is the tradename of the homopolymer obtained from N,N-dimethyl-N,N-diallylammonium chloride. 25

**The precipitate is washed with water at 50°C and then with a 50/50 mixture of acetone/water.

Composition xampl a**Examl A**

A lipstick is prepared according to the invention by mixing the following ingredients:—

5	microcrystalline wax	11 g	
	polyvinyl laurate	20 g	5
	1-docoxanoyl-3-(2-ethylhexyloxy)-propan-2-ol	20 g	
	liquid lanoline	9 g	
	castor oil	8 g	
	sesame oil	10 g	
10	acetoglycerides	9 g	10
	vaseline oil	5 g	
	oleyl alcohol	5 g	
	butylhydroxytoluene	0.2 g	
	polyethylene wax	2.8 g	
15	black iron oxide	0.2 g	15
	titanium oxide	1.1 g	
	coloured polymer according to Example 2	2.4 g	
	coloured polymer according to Example 1	6 g	
	perfume	0.8 g	

20 Example B

A rouge in the form of a compact powder is prepared by mixing the following ingredients:—

	talc	41.64 g	
	starch	10 g	
25	zinc stearate	2 g	25
	bismuth oxychloride	10 g	
	castor oil	0.7 g	
	vaseline oil	3.5 g	
	oleyl alcohol	0.6 g	
30	phytosterol	0.3 g	30
	polypeptide oleate	0.3 g	
	butylhydroxyanisole	0.01 g	
	magnesium carbonate	0.55 g	
	manganese violet	7 g	
	iron oxide	2 g	
35	titanium mica	20 g	35
	coloured polymer according to Example 1	0.5 g	
	perfume	0.4 g	
	isopropyl myristate	0.5 g	

Example C

40 A nail varnish is prepared according to the invention by mixing the following ingredients:— 40

	0.5 second nitrocellulose	12 g	
	arylsulfonamide/formaldehyde copolymer	8 g	
	camphor	2 g	
45	butyl phthalate	4 g	45
	ethyl acetate	10 g	
	toluene	20 g	
	ethyl alcohol	3 g	
	butyl alcohol	3 g	
	butyl acetate	38 g	
50	bentone 27	1 g	50
	phosphoric acid	0.01 g	
	titanium oxide	0.5 g	
	brown iron oxide	0.3 g	
	coloured polymer according to Example 3	8 g	

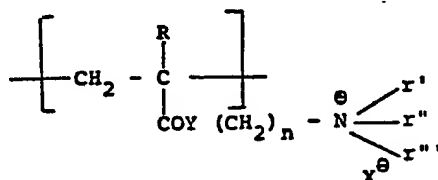
55 Claims

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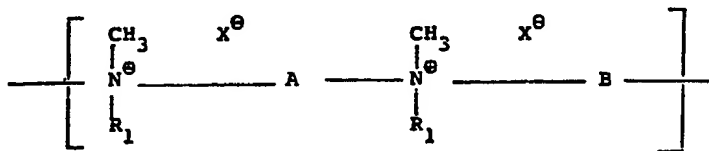
1. A cosmetic make-up composition which comprises at least one coloured pigment in a carrier or diluent, said coloured pigment being a salt obtained by reacting a polymer carrying one or more salified primary or secondary amine groups, or quarternised tertiary amine groups, with an acid dyestuff.

in the form of the free acid or a salt thereof, said dyestuff being fixed in an amount of at least 10% by weight of the stoichiometric amount.

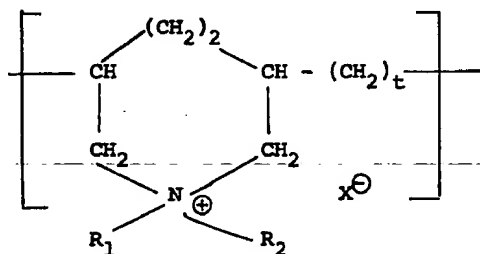
2. A composition according to claim 1 in which the acid dyestuff is a halogenoacid dyestuff.
3. A composition according to claim 2 in which the acid dyestuff is D and C Red 21, D and C Orange 5, D and C Red 27, D and C Orange 10 or D and C Red 3.
4. A composition according to claim 1 in which the acid dyestuff is an azo dyestuff.
5. A composition according to claim 4 in which the acid dyestuff is D and C Red 7, D and C Red 8, D and C Red 33, D and C Yellow 5, D and C Yellow 6, D and C Red 2 or D and C Red 4.
6. A composition according to claim 1 in which the acid dyestuff is an anthraquinone dyestuff.
7. A composition according to claim 6 in which the acid dyestuff is D and C Green 5.
8. A composition according to any one of the preceding claims, in which the said polymer is:
 - 1) a polyvinylamine salt having an average molecular weight of 1,000 to 200,000,
 - 2) a homo- or co-polymer containing units of the formula:



- 15 in which: n is 2 or 3, Y is O or NH, R represents a hydrogen atom or the CH₃ radical, r', r'' and r''', which are identical or different, represent an alkyl radical having from 1 to 6 carbon atoms, and X[⊖] is a Cl[⊖], Br[⊖] or CH₃SO₄[⊖] anion,
- 3) a polymer of the "ionene" type containing units of the following formula:



- 20 in which: A and B, which are identical or different, either represent a linear or branched alkylene radical having from 2 to 18 carbon atoms, which is optionally substituted by a hydroxyl radical and/or contains a chain oxygen atom or ureido group, or represent an o-, m- or p-xylylene group, R₁ represents an alkyl radical having from 1 to 18 carbon atoms, and X[⊖] is Cl[⊖] or Br[⊖], or
- 4) a cyclic homo- or co-polymer containing units of the following formula:



in which: l=0 or 1 such that if l=0, t=1, and if l=1, t=0, R₁ and R₂, which are identical or different, represent an alkyl radical having from 1 to 8 carbon atoms, and X[⊖]=Cl[⊖] or Br[⊖].

9. A composition according to any one of the preceding claims, in which the coloured pigment is present in an amount of 0.1 to 20% by weight based on the total weight of the composition.
10. A composition according to any one of the preceding claims, which also contains an inorganic or organic filler at a concentration of 0.1 to 40% by weight based on the total weight of the composition.
11. A composition according to any one of the preceding claims which also contains an agent for imparting pearlescence.
12. A composition according to claim 11 which contains bismuth oxychloride, titanium mica or guanine crystals.
13. A composition according to any one of the preceding claims which is in the form of a stick and contains up to 99.9% by weight of a fatty substance consisting of at least one wax and optionally at least one oil.

14. A composition according to claim 13 which contains up to 40% by weight of water, based on the total weight of the composition.
15. A composition according to any one of claims 1 to 12 which is in the form of an anhydrous or aqueous paste or cream.
- 5 16. A composition according to any one of claims 1 to 12 which is in the form of a water-in-oil or oil-in-water emulsion, the fatty phase representing from 1 to 98.8% by weight, the water phase from 1 to 98.8% and the emulsifying agent from 0.1 to 30% by weight based on the total weight of the composition. 5
- 10 17. A composition according to any one of claims 1 to 12 which is in the form of a compact or free-flowing powder and contains talc, kaolin, starch, polyethylene powder or polyamide powder as filler. 10
18. A composition according to any one of claims 1 to 12 which is in the form of a nail varnish and contains from 0.1 to 5% by weight of the coloured pigment in a nail varnish base.
- 15 19. A composition according to any one of the preceding claims which also contains one or more perfumes, antioxidants, preservatives or UV filters. 15
20. A composition according to claim 1 substantially as described in any one of Examples A to C.